

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of : KAZUTO Okamura et al.
Serial Number : 10/075,306
Filed : June 24, 2005
For : HDD SUSPENSION AND ITS MANUFACTURE
Group Art Unit : 1775

DECLARATION UNDER 37 CFR 1.132

Honorable Commissioner for Patents
Alexandria, VA. 22313-1450

Sir:

Now comes Kazuhisa Urano who declares and says that:

1. I am a co-worker of Kazuto Okamura who is an inventor of United States Patent Application Serial Number 10/075,306.
2. I graduated from Shibaura Institute of Technology, Department of Faculty of Science, Division of Applied Chemistry in 1999, and studied chemistry of organic synthesis.
3. I have been employed by Nippon Steel Chemical Co., Ltd. Since 2002, and studied polyimide synthesis for HDD suspension laminates.
4. I made a supplemental experiment to examine the alkali wet etching rates of the polyimide resin layers shown in Shimose et al (US6,203,918) and Mochizuki et al (US5,578,696) and Takabayashi et al (US5,262,227).

Experiments 1 to 7 correspond to the following.

Experiment 1: Synthetic Example 3 of Shimose et al

Experiment 2: Synthetic Example 4 of Shimose et al

Experiment 3: Synthetic Example 5 of Shimose et al

Experiment 4: Synthetic Example 6 of Shimose et al

Experiment 5: EXAMPLE 3 of Mochizuki et al

Experiment 6: EXAMPLE 7 of Mochizuki et al

Experiment 7: EXAMPLE 1 of Takabayashi et al

I did not make a supplemental experiment for EXAMPLE 1 of Mochizuki et al because 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride used in EXAMPLE 1 was not available. That is, the failure in performance of the experiment is not intentional. From the technical expertise I have gained, I can conclude that an alkali wet etching rate of polyimide synthesized from a combination of 4,4'-diaminodiphenyl and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride used in Example 1 of Mochizuki et al must be less than 0.5 μm /min.

EXPERIMENT

Experiment 1

In a 500-ml separable flask, 12.10 g (0.04139 mole) of 1,3-bis(4-aminophenoxy)benzene (APB) was dissolved in 173 g of N,N-dimethylacetamide (DMAc) with stirring. The solution was cooled in an ice bath and 14.90 g (0.04159 mole) of 3,4,3',4'-diphenylsulfonetetracarboxylic acid dianhydride (DSDA) was added with passage of a stream of nitrogen. The solution was allowed to return to room temperature and stirred continuously for 3 hours to effect polymerization. There was obtained a viscous solution of polyimide precursor C.

To measure a wet etching rate, the polyamic acid solution C was applied to a stainless foil by means of an applicator in such a manner that the solution would have a thickness of 13 μm after curing. The applied solution was dried at 110°C for 5 minutes, and was then subjected to a stepwise heat treatment for 3 minutes at each of 130°C, 160°C, 200°C, 250°C, 300°C, and 360°C. Thus, a polyimide layer was formed on the stainless foil.

Next, the polyimide layer was immersed in a 50 wt% aqueous solution of potassium hydroxide at 80°C with the stainless foil remained to carry out a wet etching test, thereby determining an etching rate. The etching rate was determined to be 0.3 $\mu\text{m}/\text{min}$.

Experiment 2

In a 500-ml separable flask, 14.09 g (0.04819 mole) of APB was dissolved in 106 g of DMAc with stirring. The solution was cooled in an ice bath and 13.81 g (0.03855 mole) of DSDA and 2.10 g (0.00964 mole) of pyromellitic acid dianhydride (PMDA) were added with passage of a stream of nitrogen. The solution was allowed to return to room temperature and stirred continuously for 3 hours to effect polymerization. There was obtained a viscous solution of polyimide precursor D.

To measure a wet etching rate, the polyamic acid solution D was applied to a stainless foil by means of an applicator in such a manner that the solution would have a thickness of 13 μm after curing. The applied solution was dried at 110°C for 5 minutes, and was then subjected to a stepwise heat treatment for 3 minutes at each of 130°C, 160°C, 200°C, 250°C, 300°C, and 360°C. Thus, a polyimide layer was formed on the stainless foil.

Next, the polyimide layer was immersed in a 50 wt% aqueous solution of potassium hydroxide at 80°C with the stainless foil remained to carry out a wet etching test, thereby determining an etching rate. The etching rate was determined to be 0.3 $\mu\text{m}/\text{min}$.

Experiment 3

In a 500-ml separable flask, 14.73 g (0.03407 mole) of bis(4-amino-phenoxyphenyl) sulfone (BAPS) was dissolved in 173 g of DMAc with stirring. The solution was cooled in an ice bath and 12.27 g (0.03424 mole) of DSDA was added with passage of a stream of nitrogen. The solution was allowed to return to room temperature and stirred continuously for 3 hours to effect polymerization. There was obtained a viscous solution of polyimide precursor E.

To measure a wet etching rate, the polyamic acid solution E was applied to a stainless foil by means of an applicator in such a manner that the solution would have a thickness of 13 μm after curing. The applied solution was dried at 110°C for 5 minutes, and was then subjected to a stepwise heat treatment for 3 minutes at each of 130°C, 160°C, 200°C, 250°C, 300°C, and 360°C. Thus, a polyimide layer was formed on the stainless foil.

Next, the polyimide layer was immersed in a 50 wt% aqueous solution of potassium hydroxide at 80°C with the stainless foil remained to carry out a wet etching test, thereby determining an etching rate. The etching rate was determined to be 0.1 $\mu\text{m}/\text{min}$.

Experiment 4

In a 500-ml separable flask, 16.83 g (0.04569 mole) of 4,4'-bis(3-amino-phenoxy)biphenyl (BAPB) was dissolved in 173 g of DMAc with stirring. The solution was cooled in an ice bath and 10.17 g (0.04661 mole) of PMDA was added with passage of a stream of nitrogen. The solution was allowed to return to room temperature and stirred continuously for 3 hours to effect polymerization. There was obtained a viscous solution of polyimide precursor F.

To measure a wet etching rate, the polyamic acid solution F was applied to a stainless foil by means of an applicator in such a manner that the solution would

have a thickness of 13 μm after curing. The applied solution was dried at 110°C for 5 minutes, and was then subjected to a stepwise heat treatment for 3 minutes at each of 130°C, 160°C, 200°C, 250°C, 300°C, and 360°C. Thus, a polyimide layer was formed on the stainless foil.

Next, the polyimide layer was immersed in a 50 wt% aqueous solution of potassium hydroxide at 80°C with the stainless foil remained to carry out a wet etching test, thereby determining an etching rate. The etching rate was determined to be less than 0.1 $\mu\text{m}/\text{min}$.

Experiment 5

255 g of DMAc were placed into a 500-ml separable flask made of glass to dissolve 25.41 g (0.06190 mol) of bis(4-(4-aminophenoxy)phenyl)propane (BAPP). 18.92 g (0.06098 mol) of 4,4'-hydroxydiphthalic anhydride (ODPA) were gradually added to the flask at room temperature, and the whole was stirred and reacted for 12 hours to prepare a polyamic acid solution A.

Next, 25.13 g (0.1220 mol) of dicyclohexyl carbodiimide were added to the resultant solution, and the whole was stirred at room temperature. Continued stirring brought the content into a "cluster" state to preclude subsequent stirring. At this time, the reaction was terminated.

To measure a wet etching rate, the polyamic acid solution A was applied to a stainless foil by means of an applicator in such a manner that the solution would have a thickness of 13 μm after curing. The applied solution was dried at 110°C for 5 minutes, and was then subjected to a stepwise heat treatment for 3 minutes at each of 130°C, 160°C, 200°C, 250°C, 300°C, and 360°C. Thus, a polyimide layer was formed on the stainless foil.

Next, the polyimide layer was immersed in a 50 wt% aqueous solution of potassium hydroxide at 80°C with the stainless foil remained to carry out a wet etching test, thereby determining an etching rate. The etching rate was determined to be 0.2 $\mu\text{m}/\text{min}$.

Experiment 6

170 g of N-methyl-pyrrolidone (NMP) were placed into a 500-ml separable flask made of glass to dissolve 15.56 g (0.04859 mol) of 2,2-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFMB). 14.44 g (0.04810 mol) of s-BPDA were gradually added to the flask at room temperature, and the whole was stirred and reacted for 12 hours to prepare a polyamic acid solution B.

Next, 13.56 ml (0.097 mol) of trifluoroacetic anhydride and 13.56 ml (0.097 mol) of triethylamine were added to the resultant solution while the solution was stirred, and the mixture was reacted at room temperature for 4 hours. After the completion of the reaction, the mixture was poured into largely excessive isopropyl alcohol and reprecipitated. The precipitated polyimide was filtered, washed with isopropyl alcohol, and dried at 40°C under reduced pressure to prepare polyisoimide powder. The polyisoimide powder was dissolved into DMAc to prepare a 20 wt% polyisoimide solution.

The polyisoimide solution was applied to a stainless foil by means of an applicator in such a manner that the solution would have a thickness of 13 μm after curing. The applied solution was dried at 110°C for 5 minutes, and was then subjected to a stepwise heat treatment for 3 minutes at each of 130°C, 160°C, 200°C, 250°C, 300°C, and 360°C. Thus, a polyimide layer was formed on the stainless foil.

Next, the polyimide layer was immersed in a 50 wt% aqueous solution of potassium hydroxide at 80°C with the stainless foil remained to carry out a wet etching test, thereby determining an etching rate. The etching rate was determined to be 0.4 $\mu\text{m}/\text{min}$.

Experiment 7

255 g of DMAc and 26.94 g (0.09156 mol) of 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) were placed into a 500-ml separable flask made of glass.

Then, 18.06 g (0.09023 mol) of 4,4'-diaminodiphenylether (DADE) were gradually added to the flask, and the whole was stirred to prepare a first aromatic polyamic acid solution having a polymer concentration of 15 wt% and a solution viscosity of 1,000 poise.

Meanwhile, 255 g of DMAc and 33.04 g (0.1123 mol) of s-BPDA were placed into a 500-ml separable flask made of glass. Then, 11.96 g (0.1106 mol) of paraphenylenediamine (PPD) were gradually added to the flask, and the whole was stirred to prepare a second aromatic polyamic acid solution having a polymer concentration of 15 wt% and a solution viscosity of 800 poise.

Each of the polyamic solutions was applied to a stainless foil (manufactured by Nippon Steel Corporation; SUS304, tension annealed product) by means of an applicator in such a manner that the solution would have a thickness of 13 μm after curing. The applied solution was dried at 110°C for 5 minutes, and was then subjected to a stepwise heat treatment for 3 minutes at each of 130°C, 160°C, 200°C, 250°C, 300°C, and 360°C. Thus, a polyimide layer was formed on the stainless foil.

Next, the polyimide layer was immersed in a 50 wt% aqueous solution of potassium hydroxide at 80°C with the stainless foil remained to carry out a wet etching test, thereby determining an etching rate.

As a result, the polyimide obtained from each of the first and second aromatic polyamic acid solutions only swelled and was not etched.

Table 1 summarizes the above results of the etching rates.

Table 1

Experiment	carboxylic dianhydride	diamine	rate of etching ($\mu\text{m}/\text{min}$)
1	DSDA	APB	0.3
2	DSDA / PMDA =80 / 20	APB	0.3
3	DSDA	BAPS	0.1
4	PMDA	BAPB	<0.1
5	ODPA	BAPP	0.2
6	s-BPDA	TFMB	0.4
7	s-BPDA	DADE	-0.4(swelled)
	s-BPDA	PPD	-2.0(swelled)

Conclusions

I can conclude as follows on the basis of the foregoing.

None of the polyimides disclosed in Examples (Synthetic Example 3, and Synthetic Example 4, and Synthetic Example 5, and Synthetic Example 6) of Shimose et al (US6,203,918) satisfies the requirement that the etching rate must be 0.5 $\mu\text{m}/\text{min}$ or more.

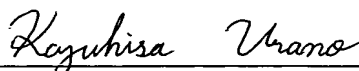
None of the polyimides disclosed in Examples of Mochizuki et al (US5,578,696) satisfies the requirement that the etching rate must be 0.5 $\mu\text{m}/\text{min}$ or more.

None of the polyimides disclosed in Examples of Takabayashi et al (US5,262,227) satisfies the requirement that the etching rate must be 0.5 $\mu\text{m}/\text{min}$ or more.

Therefore, it has been confirmed that none of Shimose et al and Mochizuki et al and Takabayashi et al discloses a polyimide layer satisfying the requirements of the present invention.

I, the undersigned petitioner, further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

This 8th day of July 2005



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